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- (54) **INERT ANODE CONTAINING OXIDES OF NICKEL, IRON AND ZINC USEFUL FOR THE ELECTROLYTIC PRODUCTION OF METALS**
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- Related U.S. Application Data**
- (63) Continuation-in-part of application No. 09/431,756, filed on Nov. 1, 1999, now Pat. No. 6,217,739, and a continuation-in-part of application No. 09/428,004, filed on Oct. 27, 1999, now Pat. No. 6,162,334, which is a continuation-in-part of application No. 09/241,518, filed on Feb. 1, 1999, now Pat. No. 6,126,799, which is a continuation-in-part of application No. 08/883,061, filed on Jun. 26, 1997, now Pat. No. 5,865,980.
- (51) **Int. Cl.**<sup>7</sup> ..... **C25B 11/04**
- (52) **U.S. Cl.** ..... **204/291; 204/243.1; 204/247.3; 205/380; 205/387; 205/392; 423/593; 423/594**
- (58) **Field of Search** ..... **204/291, 243.1, 204/247.3; 205/380, 387, 392; 423/594, 593**

(57) **ABSTRACT**

An inert anode for the electrolytic production of metals such as aluminum is disclosed. The inert anode includes a ceramic oxide material preferably made from NiO, Fe<sub>2</sub>O<sub>3</sub> and ZnO. The inert anode composition may comprise the following mole fractions of NiO, Fe<sub>2</sub>O<sub>3</sub> and ZnO: 0.2 to 0.99 NiO; 0.0001 to 0.8 Fe<sub>2</sub>O<sub>3</sub>; and 0.0001 to 0.3 ZnO. The inert anode may optionally include other oxides and/or at least one metal phase, such as Cu, Ag, Pd, Pt, Au, Rh, Ru, Ir and/or Os. The Ni—Fe—Co—O ceramic material exhibits very low solubility in Hall cell baths used to produce aluminum.

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**54 Claims, 8 Drawing Sheets**

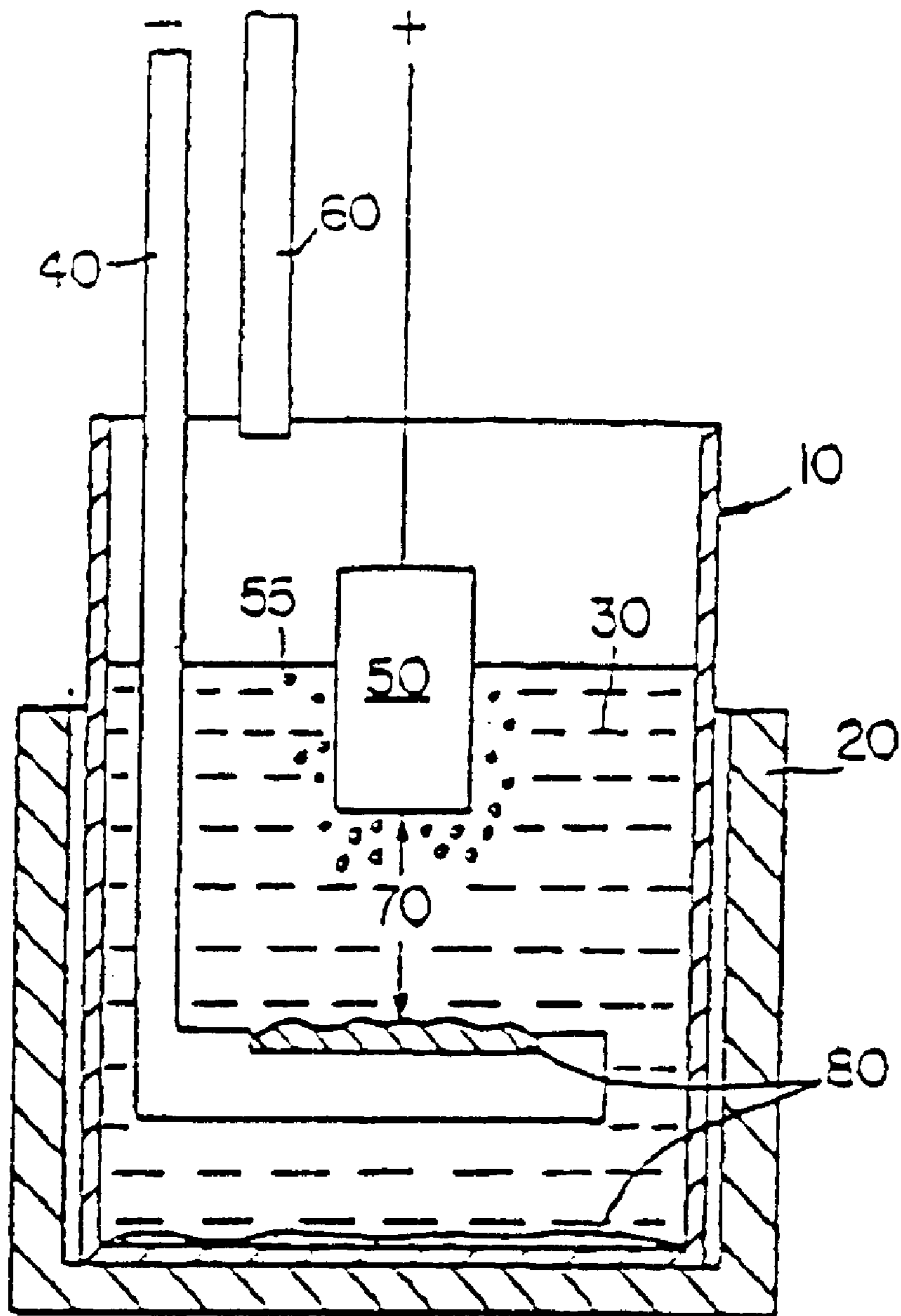


FIG. 1

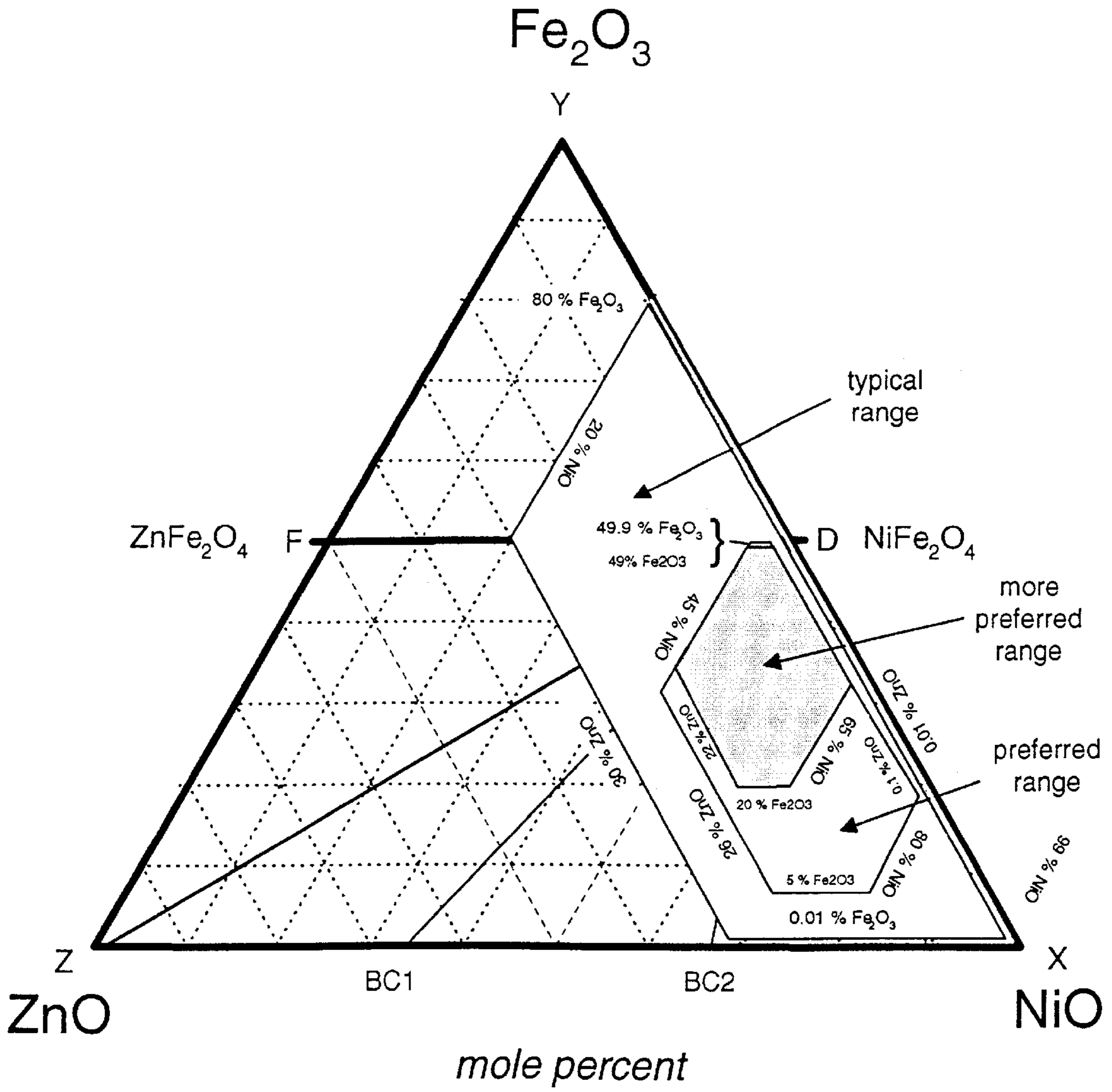


FIG. 2

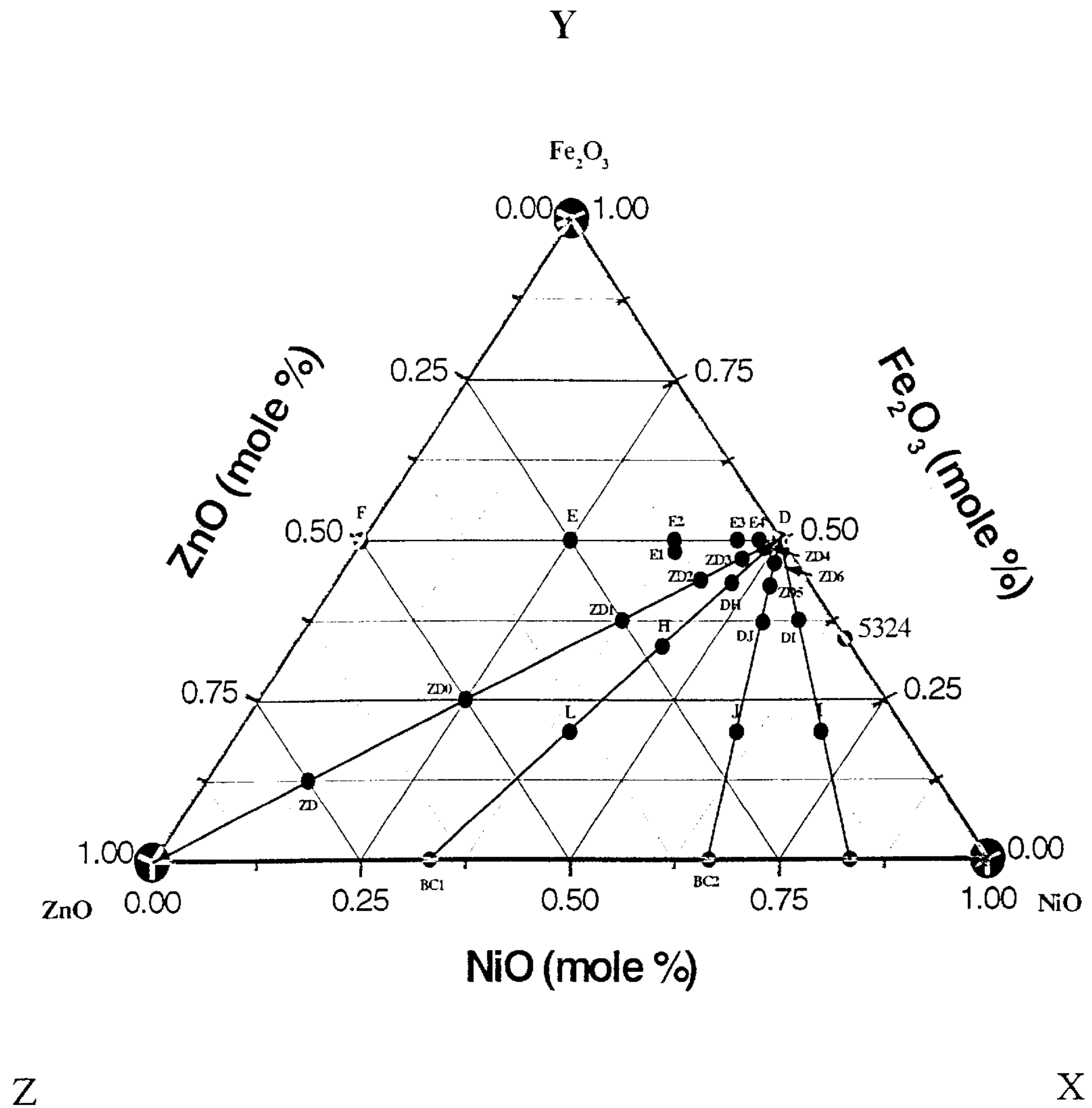


FIG. 3

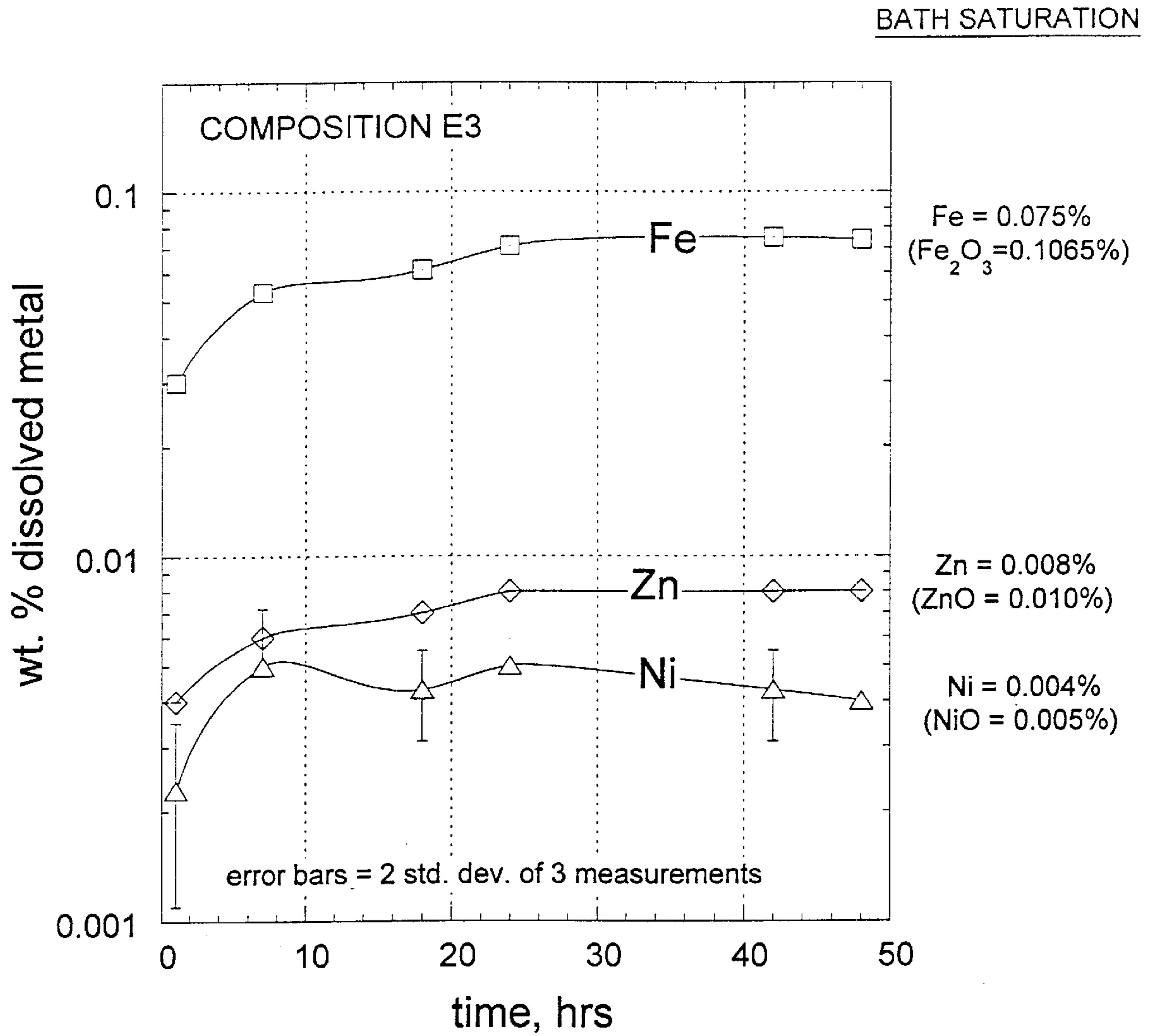


FIG. 4

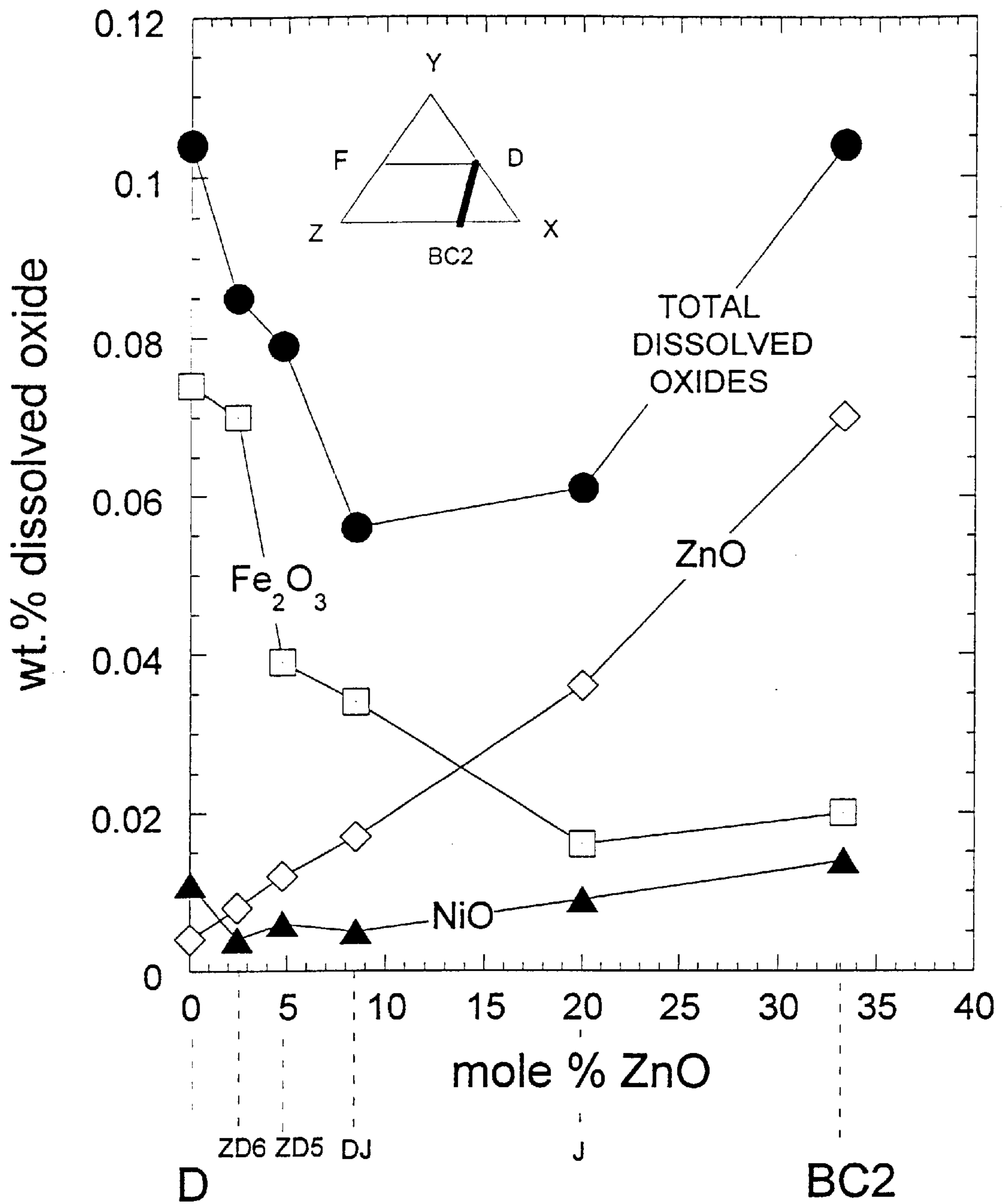


FIG. 5

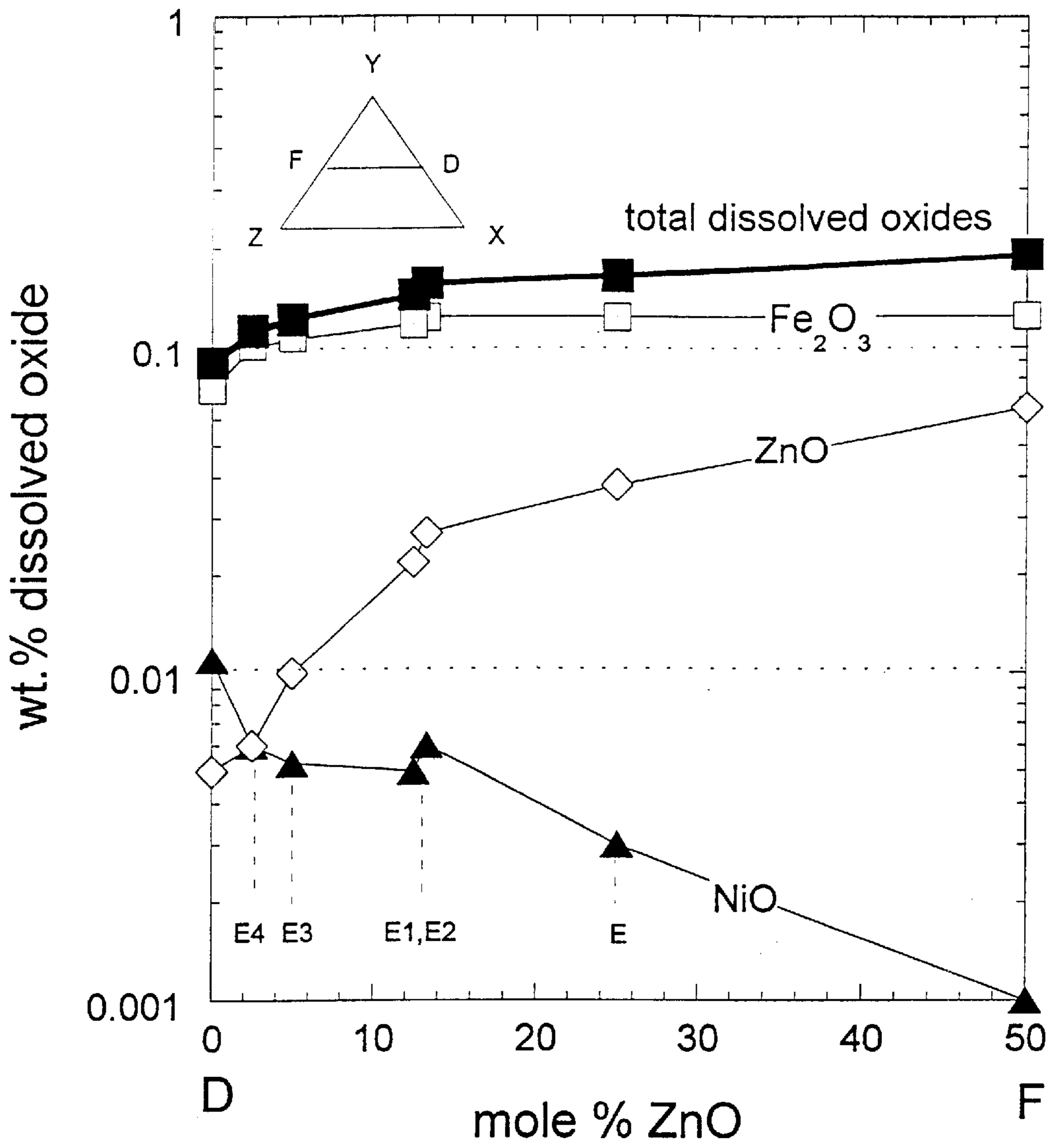


FIG. 6

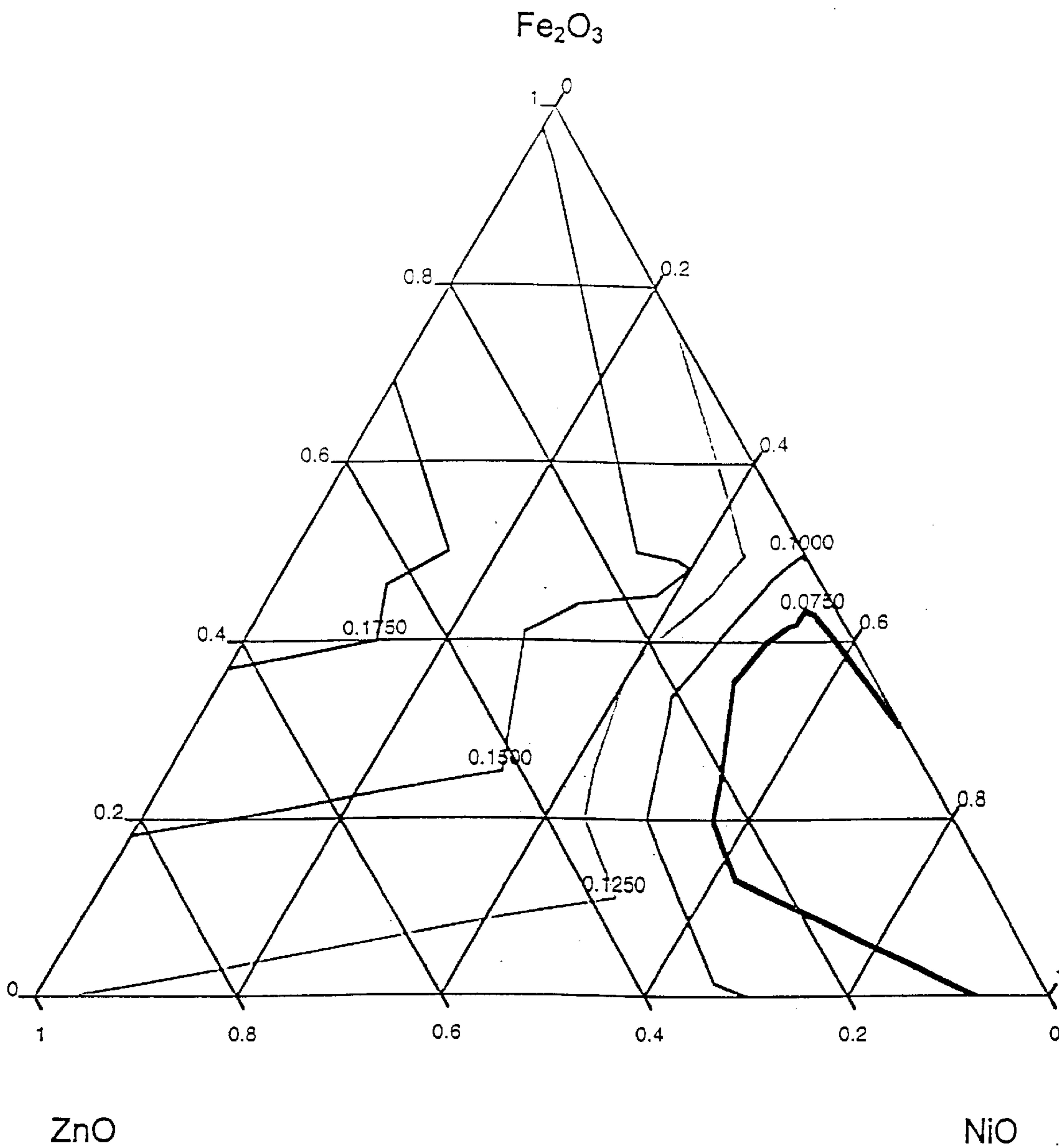


FIG. 7



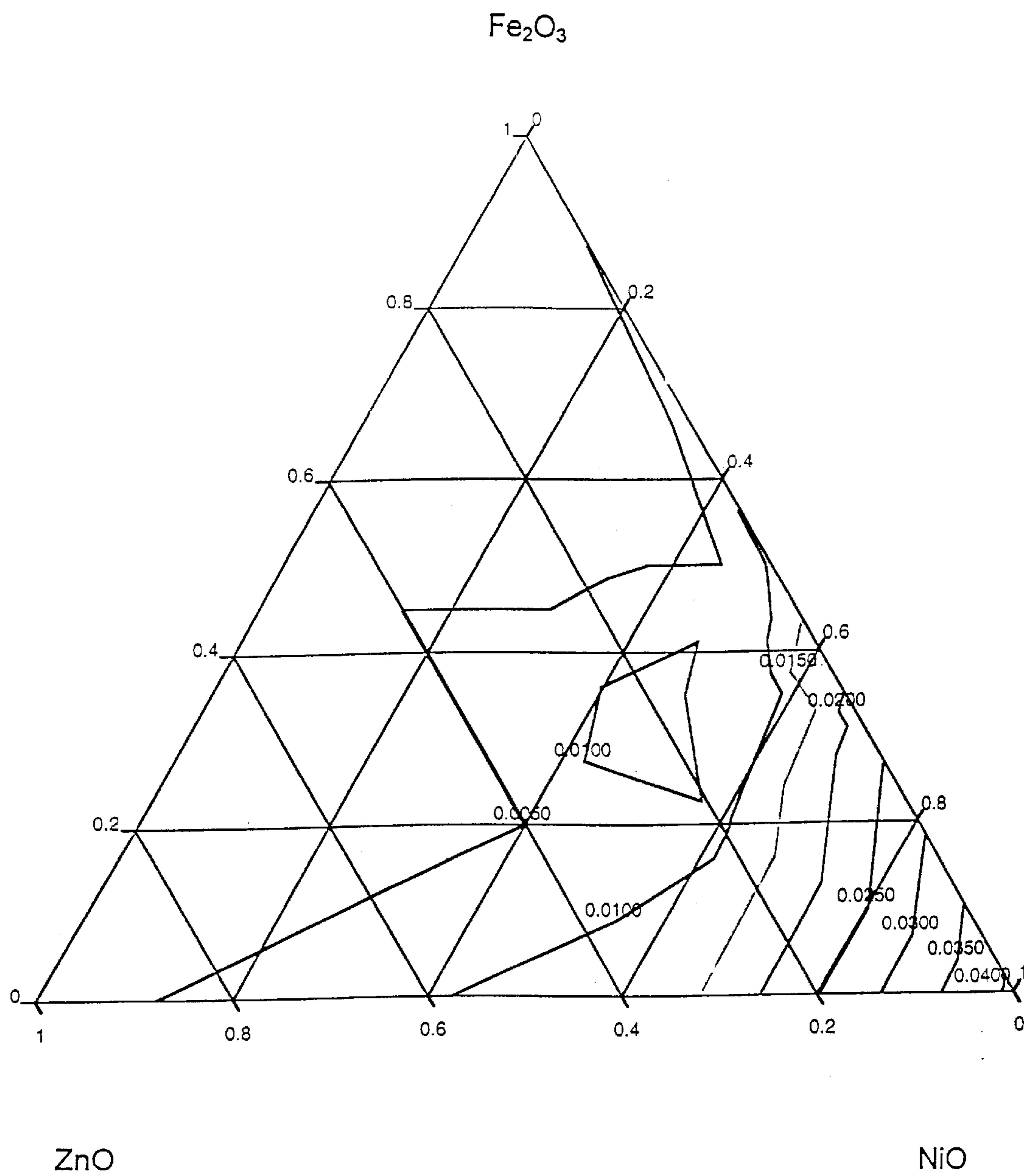


FIG. 8

# INERT ANODE CONTAINING OXIDES OF NICKEL, IRON AND ZINC USEFUL FOR THE ELECTROLYTIC PRODUCTION OF METALS

## CROSS REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of U.S. Ser. No. 09/431,756 filed Nov. 1, 1999, now U.S. Pat. No. 6,217,739 and a continuation-in-part of U.S. Ser. No. 09/428,004 filed Oct. 27, 1999, now U.S. Pat. No. 6,162,334 each of which is a continuation-in-part of U.S. Ser. No. 09/241,518 filed Feb. 1, 1999, now U.S. Pat. No. 6,126,799 which is a continuation-in-part of U.S. Ser. No. 08/883,061 filed Jun. 26, 1997, now U.S. Pat. No. 5,865,980 issued Feb. 2, 1999, each of which is incorporated herein by reference.

## GOVERNMENT CONTRACT

The United States Government has certain rights in this invention pursuant to Contract No. DE-FC07-98ID13666 awarded by the United States Department of Energy.

## FIELD OF THE INVENTION

The present invention relates to the electrolytic production of metals such as aluminum. More particularly, the invention relates to electrolysis in a cell having an inert anode comprising oxides of nickel, iron and zinc oxides.

## BACKGROUND OF THE INVENTION

The energy and cost efficiency of aluminum smelting can be significantly reduced with the use of inert, non-consumable and dimensionally stable anodes. Replacement of traditional carbon anodes with inert anodes allows a highly productive cell design to be utilized, thereby reducing capital costs. Significant environmental benefits are also possible because inert anodes produce essentially no CO<sub>2</sub> or CF<sub>4</sub> emissions. Some examples of inert anode compositions are provided in U.S. Pat. Nos. 4,374,050, 4,374,761, 4,399,008, 4,455,211, 4,582,585, 4,584,172, 4,620,905, 5,279,715, 5,794,112 and 5,865,980, assigned to the assignee of the present application. These patents are incorporated herein by reference.

A significant challenge to the commercialization of inert anode technology is the anode material. Researchers have been searching for suitable inert anode materials since the early years of the Hall-Heroult process. The anode material must satisfy a number of very difficult conditions. For example, the material must not react with or dissolve to any significant extent in the cryolite electrolyte. It must not react with oxygen or corrode in an oxygen-containing atmosphere. It should be thermally stable at temperatures of about 1,000° C. It must be relatively inexpensive and should have good mechanical strength. It must have high electrical conductivity at the smelting cell operating temperatures, e.g., about 900–1,000° C., so that the voltage drop at the anode is low.

In addition to the above-noted criteria, aluminum produced with the inert anodes should not be contaminated with constituents of the anode material to any appreciable extent. Although the use of inert anodes in aluminum electrolytic reduction cells has been proposed in the past, the use of such inert anodes has not been put into commercial practice. One reason for this lack of implementation has been the long-standing inability to produce aluminum of commercial grade purity with inert anodes. For example, impurity levels of Fe,

Cu and/or Ni have been found to be unacceptably high in aluminum produced with known inert anode materials.

The present invention has been developed in view of the foregoing, and to address other deficiencies of the prior art.

## SUMMARY OF THE INVENTION

The present invention provides an inert anode including at least one ceramic phase material which comprises oxides of nickel, iron and zinc. The inert anode may also comprise at least one metal phase including copper and/or at least one noble metal.

An aspect of the invention is to provide an inert anode composition suitable for use in a molten salt bath. The composition comprises oxides of nickel, iron and zinc of the formula Ni<sub>x</sub>Fe<sub>y</sub>Zn<sub>z</sub>O<sub>(3y+x+z)±δ</sub>, where x is the molar amount of Ni, y is the molar amount of Fe, z is the molar amount of Zn and δ is a variable which depends upon firing conditions.

Another aspect of the invention is to provide a method of making an inert anode composition. The method includes the steps of mixing iron oxide, nickel oxide and zinc oxide, or precursors of such oxides, followed by calcining the mixture to form a ceramic material of the formula Ni<sub>x</sub>Fe<sub>y</sub>Zn<sub>z</sub>O<sub>(3y+x+z)±δ</sub>, where x is the molar amount of Ni, y is the molar amount of Fe, z is the molar amount of Zn and δ is a variable which depends upon firing conditions.

Some other aspects of the invention are to provide an electrolytic cell and an electrolytic process for producing commercial purity aluminum, utilizing inert anode materials of the invention.

Additional aspects and advantages of the invention will occur to persons skilled in the art from the following detailed description.

## BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a partially schematic sectional view of an electrolytic cell for the production of aluminum including an inert anode in accordance with an embodiment of the present invention.

FIG. 2 is a ternary phase diagram illustrating ranges of nickel, iron and zinc oxides utilized in inert anode compositions of the present invention.

FIG. 3 is a ternary phase diagram indicating the amounts of nickel, iron and zinc oxides utilized in specific inert anode compositions in accordance with embodiments of the present invention.

FIG. 4 is a graph showing examples of the weight percentages of dissolved metals in a salt bath typically used in an aluminum production cell after anode compositions containing nickel oxide, iron oxide and varying amounts of zinc oxide have been exposed to the salt bath.

FIGS. 5 and 6 are graphs showing examples of the weight percentages of dissolved oxides in a salt bath typically used in an aluminum electrolytic reduction cell after anode compositions containing nickel oxide, iron oxide and varying amounts of zinc oxide have been exposed to the salt bath.

FIG. 7 is a contour plot of NiO, Fe<sub>2</sub>O<sub>3</sub> and ZnO dissolved oxides in a standard aluminum reduction salt bath for varying compositions of Ni—Fe—Zn—O anode materials.

FIG. 8 is a contour plot of NiO solubility in a standard aluminum reduction salt bath for varying compositions of Ni—Fe—Zn—O anode materials.

## DETAILED DESCRIPTION

FIG. 1 schematically illustrates an electrolytic cell for the production of aluminum which includes an inert anode in

accordance with an embodiment of the present invention. The cell includes an inner crucible **10** inside a protection crucible **20**. A cryolitic bath **30** is contained in the inner crucible **10**, and a cathode **40** is provided in the bath **30**. An inert anode **50** is positioned in the bath **30**. An alumina feed tube **60** extends partially into the inner crucible **10** above the bath **30**. The cathode **40** and inert anode **50** are separated by a distance **70** known as the anode-cathode distance (ACD). Aluminum **80** produced during a run is deposited on the cathode **40** and on the bottom of the crucible **10**. In addition to the production of aluminum, the inert anodes of the invention may also be useful in producing metals such as lead, magnesium, zinc, zirconium, titanium, lithium, calcium, silicon and the like, by electrolytic reduction of an oxide or other salt of the metal.

As used herein, the term "inert anode" means a substantially non-consumable anode which possesses satisfactory corrosion resistance and stability during the aluminum production process. The term "commercial purity aluminum" as used herein means aluminum which meets commercial purity standards upon production by an electrolytic reduction process. The commercial purity aluminum preferably comprises a maximum of 0.2 weight percent Fe, 0.1 weight percent Cu, and 0.034 weight percent Ni. In a more preferred embodiment, the commercial purity aluminum comprises a maximum of 0.15 weight percent Fe, 0.034 weight percent Cu, and 0.03 weight percent Ni. In a particularly preferred embodiment, the commercial purity aluminum comprises a maximum of 0.13 weight percent Fe, 0.03 weight percent Cu, and 0.03 weight percent Ni. The commercial purity aluminum also preferably meets the following weight percentage standards for other types of impurities: 0.2 maximum Si; 0.034 maximum Zn; and 0.03 maximum Co. The Si impurity level is more preferably kept below 0.15 or 0.10 weight percent, and the Zn level is more preferably kept below 0.03 weight percent. It is noted that for every numerical range or limit set forth herein, all numbers with the range or limit including every fraction or decimal between its stated minimum and/or maximum are considered to be designated and disclosed by this description.

Inert anodes of the present invention have at least one ceramic phase, and in a particular embodiment also have at least one metal phase. For cermets, the ceramic phase typically comprises at least 50 weight percent of the cermet, preferably from about 70 to about 90 weight percent of the cermet. At least a portion of the anode may comprise up to 100 percent of the ceramic phase. In one embodiment, the anode may comprise a cermet or metal core coated with the ceramic phase. In this embodiment, the outer ceramic layer preferably has a thickness of from 0.1 to 50 mm, more preferably from 0.2 to 5 mm.

The ceramic phase comprises oxides of nickel, iron and zinc, and is of the formula  $Ni_xFe_yZn_zO_{(3y+x+z)\pm\delta}$ , where x is the molar amount of Ni, y is the molar amount of Fe, z is the molar amount of Zn and  $\delta$  is a variable which depends upon firing conditions. In the foregoing formula, the oxygen stoichiometry is not necessarily equal to  $3y+x+z$ , but may change slightly up or down depending upon firing conditions by a factor of  $\delta$ . The value of  $\delta$  may range from 0 to 0.3, preferably from 0 to 0.2.

In the present compositions, the mole fraction of NiO typically ranges from 0.2 to 0.99, the mole fraction of  $Fe_2O_3$  typically ranges from 0.0001 to 0.8, and the mole fraction of ZnO typically ranges from 0.0001 to 0.3. In the preferred compositions, the mole fraction of NiO ranges from 0.45 to 0.8, the mole fraction of  $Fe_2O_3$  ranges from 0.05 to 0.499, and the mole fraction of ZnO ranges from 0.001 to 0.26. In

the more preferred compositions, the mole fraction of NiO ranges from 0.45 to 0.65, the mole fraction of  $Fe_2O_3$  ranges from 0.2 to 0.49, and the mole fraction of ZnO ranges from 0.001 to 0.22.

Table 1 lists the typical, preferred and more preferred mole fraction ranges of NiO,  $Fe_2O_3$  and ZnO. The listed mole fractions may be multiplied by 100 to indicate mole percentages. Within these ranges, the solubility of the constituent oxides in an electrolyte bath is reduced significantly. Lower oxide solubility in the electrolyte bath is believed to improve the purity of the aluminum produced in the bath.

TABLE 1

Mole Fractions of NiO, $Fe_2O_3$ and ZnO			
	NiO	$Fe_2O_3$	ZnO
Typical	0.2–0.99	0.0001–0.8	0.0001–0.3
Preferred	0.45–0.8	0.05–0.499	0.001–0.26
More Preferred	0.45–0.65	0.2–0.49	0.001–0.22

FIG. 2 is a ternary phase diagram illustrating the typical, preferred and more preferred ranges of NiO,  $Fe_2O_3$  and ZnO starting materials used to make inert anode compositions in accordance with embodiments of the present invention. Although the mole percentages illustrated in FIG. 2 are based on NiO,  $Fe_2O_3$  and ZnO starting materials, other nickel, iron, and zinc oxides, or compounds which form oxides upon calcination, may be used as starting materials in accordance with the present invention.

Table 2 lists some ternary Ni—Fe—Zn—O materials that may be suitable for use as the ceramic phase of the present inert anodes, as well as some comparison materials. In addition to the phases listed in Table 2, minor or trace amounts of other phases may be present.

TABLE 2

Ni—Fe—Zn—O Compositions			
Sample I.D.	Nominal Composition	Measured Elemental Weight Percent Fe, Ni, Zn	Structural Types (identified by XRD)
5412	NiFe <sub>2</sub> O <sub>4</sub>	48, 23.0, 0.15	NeFe <sub>2</sub> O <sub>4</sub>
5324	NiFe <sub>2</sub> O <sub>4</sub> + NiO	34, 36, 0.06	NiFe <sub>2</sub> O <sub>4</sub> , NiO
E4	Zn <sub>0.05</sub> Ni <sub>0.95</sub> Fe <sub>2</sub> O <sub>4</sub>	43, 22, 1.4	NiFe <sub>2</sub> O <sub>4</sub>
E3	Zn <sub>0.1</sub> Ni <sub>0.9</sub> Fe <sub>2</sub> O <sub>4</sub>	43, 20, 2.7	NiFe <sub>2</sub> O <sub>4</sub>
E2	Zn <sub>0.25</sub> Ni <sub>0.75</sub> Fe <sub>2</sub> O <sub>4</sub>	40, 15, 5.9	NiFe <sub>2</sub> O <sub>4</sub>
E1	Zn <sub>0.25</sub> Ni <sub>0.75</sub> Fe <sub>1.9</sub> O <sub>4</sub>	45, 18, 7.8	NiFe <sub>2</sub> O
E	Zn <sub>0.5</sub> Ni <sub>0.5</sub> Fe <sub>2</sub> O <sub>4</sub>	45, 12, 13	(ZnNi)Fe <sub>2</sub> O <sub>4</sub> , ZnO <sup>S</sup>
F	ZnFe <sub>2</sub> O <sub>4</sub>	43, 0.03, 24	ZnFe <sub>2</sub> O <sub>4</sub> , ZnO
H	Zn <sub>0.5</sub> NiFe <sub>1.5</sub> O <sub>4</sub>	33, 23, 13	(ZnNi)Fe <sub>2</sub> O <sub>4</sub> , NiO <sup>S</sup>
J	Zn <sub>0.5</sub> Ni <sub>1.5</sub> FeO <sub>4</sub>	26, 39, 10	NiFe <sub>2</sub> O <sub>4</sub> , NiO
L	ZnNiFeO <sub>4</sub>	22, 23, 27	(ZnNi)Fe <sub>2</sub> O <sub>4</sub> , NiO <sup>S</sup> , ZnO
ZD6	Zn <sub>0.05</sub> Ni <sub>1.05</sub> Fe <sub>1.9</sub> O <sub>4</sub>	40, 24, 1.3	NiFe <sub>2</sub> O <sub>4</sub>
ZD5	Zn <sub>0.1</sub> Ni <sub>1.1</sub> Fe <sub>1.8</sub> O <sub>4</sub>	29, 18, 2.3	NiFe <sub>2</sub> O <sub>4</sub>
ZD3	Zn <sub>0.12</sub> Ni <sub>0.94</sub> Fe <sub>1.88</sub> O <sub>4</sub>	43, 23, 3.2	NiFe <sub>2</sub> O <sub>4</sub>
ZD1	Zn <sub>0.5</sub> Ni <sub>0.75</sub> Fe <sub>1.5</sub> O <sub>4</sub>	40, 20, 11	(ZnNi)Fe <sub>2</sub> O <sub>4</sub>
DH	Zn <sub>0.18</sub> Ni <sub>0.96</sub> Fe <sub>1.8</sub> O <sub>4</sub>	42, 23, 4.9	NiFe <sub>2</sub> O <sub>4</sub> , NiO
DI	Zn <sub>0.08</sub> Ni <sub>1.17</sub> Fe <sub>1.5</sub> O <sub>4</sub>	38, 30, 2.4	NiFe <sub>2</sub> O <sub>4</sub> , NiO
DJ	Zn <sub>0.17</sub> Ni <sub>1.1</sub> Fe <sub>1.5</sub> O <sub>4</sub>	36, 29, 4.8	NiFe <sub>2</sub> O <sub>4</sub> , NiO
BC2	Zn <sub>0.33</sub> Ni <sub>0.67</sub> O	0.11, 52, 25	NiO <sup>S</sup>

<sup>S</sup>means shifted peak.

FIG. 3 is a ternary phase diagram illustrating the amounts of NiO,  $Fe_2O_3$  and ZnO starting materials used to make the compositions listed in Table 2, which may be used alone or as the ceramic phase(s) of cermet inert anodes. Such inert anodes may in turn be used to produce commercial purity aluminum in accordance with the present invention.

The oxide compositions listed in Table 2 and shown in FIG. 3 may be prepared and tested as follows. Oxide powders are synthesized by a wet chemical approach. The starting chemicals include one or a mixture of chlorides, acetates, nitrates, tartarates, citrates and sulfates of Ni, Fe and Zn salts. Chlorides, acetates and nitrates of Ni, Fe and Zn salts are preferred precursors. Such precursors are commercially available from sources such as Aldrich and Fisher. A homogeneous solution is prepared by dissolving the desired amounts of the chemicals into deionized water. The solution pH is adjusted to 6–9 by adding ammonium hydroxide while stirring. A pH of from 7 to 8 is preferred. The viscous solution is dried by oven, freeze dryer, spray dryer or the like. The resultant dried solid is amorphous. Crystalline oxide powders are obtained after calcination of the dried solid, e.g., at a temperature of from 600 to 800° C. for 2 hours. The oxide powders are then uniaxially or isostatically pressed to pellet form under a pressure of from 10,000 to 30,000 psi, typically 20,000 psi. The pressed pellets are sintered in air at a temperature of 1,000–1500° C., typically 1200° C., for 24 hours. The crystalline structure and the composition of the sintered oxide pellets may be analyzed by x-ray diffraction (XRD) and inductively-coupled plasma (ICP) techniques.

The solubilities of Ni—Fe—Zn—O anode compositions of the invention were tested. The solubility of each ceramic mixture was measured by holding approximately 3 g of sintered oxide pellets in 160 g of a standard cryolitic molten salt bath at 960° C. for 96 hours. The standard salt bath was contained in a platinum crucible and prepared by batching NaF, AlF<sub>3</sub>, Greenland cryolite, CaF<sub>2</sub> and A<sub>2</sub>O<sub>3</sub> so that NaF:AlF<sub>3</sub>=1.1, Al<sub>2</sub>=5 weight percent, and CaF<sub>2</sub>=5 weight. In these experiments, dried air was circulated over the salt

bath at a low flow rate of 100 cm<sup>3</sup>/min, as well as periodically bubbled into the molten salt to maintain oxidizing conditions. Samples of the melt were withdrawn periodically for chemical bath analysis.

FIG. 4 shows Fe, Zn and Ni impurity levels periodically measured for composition E3. After 50 hours, the Fe solubility was 0.075 weight percent, which translates to an Fe<sub>2</sub>O<sub>3</sub> solubility of 0.1065 weight percent. The solubility of Zn was 0.008 weight percent, which corresponds to a ZnO solubility of 0.010 weight percent. The solubility of Ni was 0.004 weight percent, which translates to a NiO solubility of 0.005 weight percent.

When the foregoing solubility test method is used, the weight percent of total dissolved oxides is preferably below 0.1 weight percent, more preferably below 0.08 weight percent. The amount of total dissolved oxides, i.e., Fe<sub>2</sub>O<sub>3</sub>, NiO and ZnO, as measured by the foregoing procedure, is defined herein as the “Hall cell bath solubility.” The Hall cell bath solubility of the present compositions, is preferably below the solubility of stoichiometric nickel ferrite.

Table 3 lists the nominal composition of each sample tested, the average weight percent of dissolved metal (Fe, Ni and Zn) in the electrolyte bath, and the average weight percent of dissolved oxide (Fe<sub>2</sub>O<sub>3</sub>, NiO and ZnO) in the electrolyte bath. The dissolved metal and oxide levels were determined after the bath composition had reached saturation with the components of the oxide test samples. The results are also expressed as bath oxide saturation values. The total dissolved oxide content of the bath is the sum of the oxide saturation values, with a low total dissolved oxide content being desirable.

TABLE 3

Ceramic Phase Solubility in Standard Salt Bath at 960° C.								
Nominal Composition	Sample ID	Average weight percent dissolved metal			Average weight percent dissolved oxide			
		Fe	Ni	Zn	Fe <sub>2</sub> O <sub>3</sub>	NiO	ZnO	Total
NiO	X	0.014*	0.032	<0.004*	0.020*	0.041	0.006*	0.068
Fe <sub>2</sub> O <sub>3</sub>	Z	0.097	Na	Na	0.139	0.003*	0.006*	0.148
NiFe <sub>2</sub> O <sub>4</sub>	5412 (D)	0.052	0.009	0.004	0.074	0.011	0.005*	0.090
NiFe <sub>2</sub> O <sub>4</sub> + NiO	5324	0.033	0.018	<0.004*	0.047	0.023	0.006*	0.076
ZnO	Y	Na	na	0.082	0.020*	0.003*	0.102	0.125
ZnFe <sub>2</sub> O <sub>4</sub>	Y	Na	na	0.085	0.020*	0.003*	0.106	0.129
ZnFe <sub>2</sub> O <sub>4</sub>	F	0.075	na	0.039	0.107	0.003*	0.049	0.159
ZnFe <sub>2</sub> O <sub>4</sub>	F	0.087	<0.001*	0.052	0.124	<0.001	0.065	0.190
Ni <sub>0.67</sub> Zn <sub>0.33</sub> O	BC2	na	0.033	0.053	0.020*	0.042	0.066	0.128
Ni <sub>0.67</sub> Zn <sub>0.33</sub> O	BC2	na	0.011	0.056	0.020*	0.014	0.070	0.104
Ni <sub>0.5</sub> Zn <sub>0.5</sub> Fe <sub>2</sub> O <sub>4</sub>	E	0.086	0.002	0.031	0.123	0.003	0.038	0.164
Ni <sub>0.75</sub> Zn <sub>0.25</sub> Fe <sub>1.90</sub> O <sub>4</sub>	E1	0.086	0.005	0.022	0.123	0.006	0.027	0.156
Ni <sub>0.75</sub> Zn <sub>0.25</sub> Fe <sub>2</sub> O <sub>4</sub>	E2	0.082	0.004	0.018	0.117	0.005	0.022	0.144
Ni <sub>0.90</sub> Zn <sub>0.10</sub> Fe <sub>2</sub> O <sub>4</sub>	E3	0.075	0.004	0.008	0.107	0.005	0.010	0.122
Ni <sub>0.95</sub> Zn <sub>0.05</sub> Fe <sub>2</sub> O <sub>4</sub>	E4	0.070	0.004	0.005	0.100	0.006	0.006	0.112
NiZnFeO <sub>4</sub>	L	0.006	0.004	0.102	0.009	0.005	0.127	0.141
NiZnO <sub>0.5</sub> Fe <sub>1.5</sub> O <sub>4</sub>	H	0.018	0.011	0.052	0.026	0.014	0.065	0.105
Ni <sub>1.5</sub> Zn <sub>0.5</sub> FeO <sub>4</sub>	J	0.011	0.007	0.029	0.016	0.009	0.036	0.061
Ni <sub>1.05</sub> Zn <sub>0.05</sub> Fe <sub>1.9</sub> O <sub>4</sub>	ZD6	0.049	0.004	0.008	0.070	0.004	0.008	0.085
NiFe <sub>2</sub> O <sub>4</sub> + 5% ZnO	—	0.054	0.005	0.014	0.077**	0.006	0.017**	0.100
Ni <sub>0.95</sub> Zn <sub>0.12</sub> Fe <sub>1.9</sub> O <sub>4</sub>	—	0.034	0.008	0.014	0.049	0.010	0.018	0.077
Ni <sub>0.94</sub> Zn <sub>0.12</sub> Fe <sub>1.88</sub> O <sub>4</sub>	ZD3	0.062**	0.005	0.010	0.089**	0.006	0.012	>0.107
Ni <sub>0.94</sub> Zn <sub>0.12</sub> Fe <sub>1.88</sub> O <sub>4</sub>	ZD3	0.044**	0.005	0.019	0.063**	0.006	0.024	>0.093
Ni <sub>1.17</sub> Zn <sub>0.08</sub> Fe <sub>1.50</sub> O <sub>4</sub>	DI	0.019	0.012	0.009	0.027	0.015	0.011	0.053
Ni <sub>0.75</sub> Zn <sub>0.50</sub> Fe <sub>1.50</sub> O <sub>4</sub>	ZD1	0.052	0.065	0.042	0.074	0.008	0.052	0.134
Ni <sub>1.10</sub> Zn <sub>0.17</sub> Fe <sub>1.50</sub> O <sub>4</sub>	DJ	0.024	0.004	0.014	0.034	0.005	0.017	0.056
Ni <sub>0.96</sub> Zn <sub>0.17</sub> Fe <sub>1.50</sub> O <sub>4</sub>	DH	0.044	0.007	0.022	0.063	0.009	0.027	0.099
Ni <sub>1.10</sub> Zn <sub>0.10</sub> Fe <sub>1.80</sub> O <sub>4</sub>	ZD5	0.039	0.006	0.012	0.056	0.0076	0.015	0.079

NOTES: na = not analyzed, \*means-at salt-background level; \*\*means did not reach saturation after 96 hrs.

FIGS. 5 and 6 graphically illustrate the amount of dissolved oxides for samples comprising varying amounts of NiO, Fe<sub>2</sub>O<sub>3</sub> and ZnO. The compositions shown in FIG. 5 exhibit very low oxide dissolution, particularly for compositions containing from 1 to 30 mole percent ZnO. Zinc oxide concentrations of from 5 to 25 mole percent exhibit extremely low oxide solubility. The compositions illustrated in FIG. 5 fall along the line from point BC2 to point D in FIG. 3. The compositions shown in FIG. 6 exhibit higher oxide solubility compared with the compositions of FIG. 5. The compositions of FIG. 6 fall along the spinel line from point F to point D in FIG. 3. Unlike compositions falling along the line BC2-D, those along the line D-F exhibit no minimum in oxide solubility, as illustrated in FIG. 6. The total dissolved oxide content of the bath increases as the composition of the oxide moves from NiFe<sub>2</sub>O<sub>4</sub> to ZnFe<sub>2</sub>O<sub>4</sub>. The improved oxide compositions of the present invention which exhibit substantially lower electrolyte solubility are shown in the compositional regions of FIG. 2.

Commercially available software (JMP) was used to fit contours of the solubility results listed in Table 3. FIG. 7 is a contour plot of total dissolved oxides (NiO, Fe<sub>2</sub>O<sub>3</sub> and ZnO) for ceramic anode compositions comprising varying amounts of NiO, Fe<sub>2</sub>O<sub>3</sub> and ZnO. A region in which the level of total dissolved oxides is below 0.10 weight percent is illustrated in FIG. 7, as well as a region in which the level of total dissolved oxides is less than 0.075 weight percent.

FIG. 8 is a contour plot of dissolved NiO for ceramic anode compositions comprising varying amounts of NiO, Fe<sub>2</sub>O<sub>3</sub> and ZnO. As shown in the lower right corner of the diagram of FIG. 8, ceramic anode compositions which are NiO-rich yield the highest levels of dissolved NiO. For example, regions in which the levels of dissolved NiO are greater than 0.025, 0.030, 0.035 and 0.040 weight percent are illustrated in FIG. 8. Such high levels of dissolved NiO are particularly disadvantageous during the production of commercial purity aluminum because the commercial purity standards which dictate the maximum allowable amounts of nickel impurities are very stringent, e.g., 0.03 or 0.34 weight percent maximum Ni. The preferred inert anode compositions of the present invention not only exhibit substantially reduced total oxide solubilities, but also exhibit substantially reduced NiO solubilities.

In an embodiment of the invention, in addition to the Ni—Fe—Zn—O ceramic phase(s), the inert anodes may include at least one metal phase. The metal phase may include, for example, a base metal and at least one noble metal. Copper and silver are preferred base metals. However, other electrically conductive metals may optionally be used to replace all or part of the copper or silver. Furthermore, additional metals such as Co, Ni, Fe, Al, Sn, Nb, Ta, Cr, Mo, W and the like may be alloyed with the base metal. Such base metals may be provided from individual or alloyed powders of the metals, or as oxides of such metals.

The noble metal preferably comprises at least one metal selected from Ag, Pd, Pt, Au, Rh, Ru, Ir and Os. More preferably, the noble metal comprises Ag, Pd, Pt, Ag and/or Rh. Most preferably, the noble metal comprises Ag, Pd or a combination thereof. The noble metal may be provided from individual or alloyed powders of the metals, or as oxides of such metals, e.g., silver oxide, palladium oxide, etc.

Preferably, metal phase(s) of the inert electrode comprises at least about 60 weight percent of the combined base metal and noble metal, more preferably at least about 80 weight percent. The presence of base metal/noble metal provides high levels of electrical conductivity through the inert elec-

trodes. The base metal/noble metal phase may form either a continuous phase(s) within the inert electrode or a discontinuous phase(s) separated by the oxide phase(s).

The metal phase of the inert electrode typically comprises from about 50 to about 99.99 weight percent of the base metal, and from about 0.01 to about 50 weight percent of the noble metal(s). Preferably, the metal phase comprises from about 70 to about 99.95 weight percent of the base metal, and from about 0.05 to about 30 weight percent of the noble metal(s). More preferably, the metal phase comprises from about 90 to about 99.9 weight percent of the base metal, and from about 0.1 to about 10 weight percent of the noble metal(s).

The types and amounts of base and noble metals contained in the metal phase of the inert anode are selected in order to substantially prevent unwanted corrosion, dissolution or reaction of the inert electrodes, and to withstand the high temperatures which the inert electrodes are subjected to during the electrolytic metal reduction process. For example, in the electrolytic production of aluminum, the production cell typically operates at sustained smelting temperatures above 800° C., usually at temperatures of 900–980° C. Accordingly, inert anodes used in such cells should preferably have melting points above 800° C., more preferably above 900° C., and optimally above about 1,000° C.

In one embodiment of the invention, the metal phase comprises copper as the base metal and a relatively small amount of silver as the noble metal. In this embodiment, the silver content is preferably less than about 10 weight percent, more preferably from about 0.2 to about 9 weight percent, and optimally from about 0.5 to about 8 weight percent, remainder copper. By combining such relatively small amounts of Ag with such relatively large amounts of Cu, the melting point of the Cu—Ag alloy phase is significantly increased relative to the eutectic point. For example, an alloy comprising 95 weight percent Cu and 5 weight percent Ag has a melting point of approximately 1,000° C., while an alloy comprising 90 weight percent Cu and 10 weight percent Ag forms a eutectic having a melting point of approximately 780° C. This difference in melting points is particularly significant where the alloys are to be used as part of inert anodes in electrolytic aluminum reduction cells, which typically operate at smelting temperatures of greater than 800° C.

In another embodiment of the invention, the metal phase comprises copper as the base metal and a relatively small amount of palladium as the noble metal. In this embodiment, the Pd content is preferably less than about 20 weight percent, more preferably from about 0.1 to about 10 weight percent.

In a further embodiment of the invention, the metal phase comprises silver as the base metal and a relatively small amount of palladium as the noble metal. In this embodiment, the Pd content is preferably less than about 50 weight percent, more preferably from about 0.05 to about 30 weight percent, and optimally from about 0.1 to about 20 weight percent. Alternatively, silver may be used alone as the metal phase of the anode.

In another embodiment of the invention, the metal phase comprises Cu, Ag and Pd. In this embodiment, the amounts of Cu, Ag and Pd are preferably selected in order to provide an alloy having a melting point above 800° C., more preferably above 900° C., and optimally above about 1,000° C. The silver content is preferably from about 0.5 to about 30 weight percent of the metal phase, while the Pd content is preferably from about 0.01 to about 10 weight percent.

More preferably, the Ag content is from about 1 to about 20 weight percent of the metal phase, and the Pd content is from about 0.1 to about 10 weight percent. The weight ratio of Ag to Pd is preferably from about 2:1 to about 100:1, more preferably from about 5:1 to about 20:1.

In accordance with a preferred embodiment of the present invention, the types and amounts of base and noble metals contained in the metal phase are selected such that the resultant material forms at least one alloy phase having an increased melting point above the eutectic melting point of the particular alloy system. For example, as discussed above in connection with the binary Cu—Ag alloy system, the amount of the Ag addition may be controlled in order to substantially increase the melting point above the eutectic melting point of the Cu—Ag alloy. Other noble metals, such as Pd and the like, may be added to the binary Cu—Ag alloy system in controlled amounts in order to produce alloys having melting points above the eutectic melting points of the alloy systems. Thus, binary, ternary, quaternary, etc. alloys may be produced in accordance with the present invention having sufficiently high melting points for use as part of inert electrodes in electrolytic metal production cells.

The inert anodes may be formed by techniques such as powder sintering, sol-gel processing, slip casting and spray forming. Preferably, the inert anodes are formed by powder techniques in which powders comprising the oxides and optional metals are pressed and sintered.

The inert anode may comprise a monolithic component of such materials, or may comprise a substrate having at least one coating or layer of such material.

Prior to combining the ceramic and metal powders, the ceramic powders, such as NiO, Fe<sub>2</sub>O<sub>3</sub> and ZnO, may be blended in a mixer. Optionally, the blended ceramic powders may be ground to a smaller size before being transferred to a furnace where they are calcined, e.g., for 12 hours at 1,250° C. The calcination produces a mixture made from oxide phases, for example, as illustrated in FIGS. 2 and 3. If desired, the mixture may include other oxide powders and/or oxide-forming metal powders such as Al. Additional oxide powders may include oxides of metals from Groups IIA to VA and IB to VIIIB of the Periodic Table, as well as rare earth metals and the like. For example, Cr<sub>2</sub>O<sub>3</sub>, Co<sub>3</sub>O<sub>4</sub> and/or CoO may be used as additional oxides. As an alternative to the use of mixed metal oxides as the starting materials, the oxide powder may be formed by wet chemical methods utilizing precursors of the constituent oxides, such as the chlorides, acetates, nitrates, etc. of Ni, Fe and Zn salts as described previously.

The calcined oxide mixture may be ground to an average particle size of approximately 10 microns, e.g., in a ball mill. The fine oxide particles are blended with a polymeric binder and water to make a slurry. The slurry may contain about 60 weight percent solids and about 40 weight percent water. Spray drying the slurry produces dry agglomerates of the oxides that may be transferred to a V-blender and optionally mixed with metal powders. The metal powders may comprise substantially pure metals and alloys thereof, or may comprise oxides of a base metal and/or a noble metal.

In a preferred embodiment, about 1–10 parts by weight of an organic polymeric binder are added to 100 parts by weight of the metal oxide and optional metal particles. Some suitable binders include polyvinyl alcohol, acrylic polymers, polyglycols, polyvinyl acetate, polyisobutylene, polycarbonates, polystyrene, polyacrylates, and mixtures and copolymers thereof. Preferably, about 3–6 parts by weight of the binder are added to 100 parts by weight of the oxide and metal mixture.

The V-blended mixture of oxide and optional metal powders may be sent to a press where it is isostatically pressed, for example at 10,000 to 60,000 psi, into anode shapes. A pressure of about 20,000 psi is particularly suitable for many applications. The pressed shapes may be sintered in a controlled atmosphere furnace supplied with an argon-oxygen gas mixture. Sintering temperatures of 1,000–1,400° C. may be suitable. The furnace is typically operated at 1,350–1,385° C. for 2–4 hours. The sintering process burns out any polymeric binder from the anode shapes and reduces the porosity of the pressed body.

The gas supplied during sintering preferably contains about 5–3,000 ppm oxygen, more preferably about 5–700 ppm and most preferably about 10–350 ppm. Lesser concentrations of oxygen result in a product having a larger metal phase than desired, and excessive oxygen results in a product having too much of the phase containing metal oxides (ceramic phase). The remainder of the gaseous atmosphere preferably comprises a gas such as argon that is inert to the metal at the reaction temperature.

Sintering anode compositions in an atmosphere of controlled oxygen content typically lowers the porosity to acceptable levels and avoids bleed out of any metal phase. The atmosphere may be predominantly argon, with controlled oxygen contents in the range of 17 to 350 ppm. Anode compositions sintered under these conditions typically have less than 0.5 percent porosity when the compositions are sintered in argon containing 70–150 ppm oxygen. The anodes may optionally be densified by hot pressing or hot isostatic pressing.

The sintered anode may be connected to a suitable electrically conductive support member within an electrolytic metal production cell by means such as welding, diffusion welding, brazing, mechanically fastening, cementing and the like.

The inert anode may include a ceramic described above successively connected in series to a transition cermet region and a nickel end. A nickel or nickel-chromium alloy rod may be welded to the nickel end. The transition region, for example, may include four layers of graded composition, ranging from 25 weight percent Ni adjacent the ceramic or cermet end and then 50, 75 and 100 weight percent Ni, balance the mixture of oxide and optional metal powders described above.

Several cermet inert anode compositions comprising both ceramic and metal phases were prepared in accordance with the procedures described above having diameters of about 5/8 inch and length of about 5 inches. These compositions were evaluated in a Hall-Heroult test cell similar to that schematically illustrated in FIG. 1. The cell was operated for 100 hours at 960° C., with an aluminum fluoride to sodium fluoride bath ratio of 1.1 and alumina concentration maintained at about 7–7.5 weight percent. The anode compositions and impurity concentrations in aluminum produced by the cell are shown in Table 4. The impurity values shown in Table 4 represent the average of four test samples of the produced metal taken at four different locations after the 100 hour test period. Interim samples of the produced aluminum were consistently below the final impurity levels listed.

TABLE 4

Impurity Levels of Aluminum Produced with Various Anode Compositions		Porosity	Fe	Cu	Ni
1	3Ag—14Cu—42.9NiO—40.1Fe <sub>2</sub> O <sub>3</sub>		0.191	0.024	0.044
2	3Ag—14Cu—42.9NiO—40.1Fe <sub>2</sub> O <sub>3</sub>		0.26	0.012	0.022
3	3Ag—14Cu—26.45NiO—56.55Fe <sub>2</sub> O <sub>3</sub>		0.375	0.13	0.1
4	3Ag—14Cu—42.9NiO—40.1Fe <sub>2</sub> O <sub>3</sub>		0.49	0.05	0.085
5	3Ag—14Cu—42.9NiO—40.1Fe <sub>2</sub> O <sub>3</sub>		0.36	0.034	0.027
6	5Ag—10Cu—43.95NiO—41.05Fe <sub>2</sub> O <sub>3</sub>		0.4	0.06	0.19
7	3Ag—14Cu—42.9NiO—40.1Fe <sub>2</sub> O <sub>3</sub>		0.38	0.095	0.12
8	2Ag—15Cu—42.9NiO—40.1Fe <sub>2</sub> O <sub>3</sub>		0.5	0.13	0.33
9	2Ag—15Cu—42.9NiO—40.1Fe <sub>2</sub> O <sub>3</sub>		0.1	0.16	0.26
10	3Ag—11Cu—44.46NiO—41.54Fe <sub>2</sub> O <sub>3</sub>		0.14	0.017	0.13
11	1Ag—14Cu—27.75NiO—57.25Fe <sub>2</sub> O <sub>3</sub>		0.24	0.1	0.143
12	1Ag—14Cu—27.96NiO—57.04Fe <sub>2</sub> O <sub>3</sub>	0.127	0.07	0.011	0.0212
13	1Ag—14Cu—27.96NiO—57.04Fe <sub>2</sub> O <sub>3</sub>	0.168	0.22	0.04	0.09
14	1Ag—14Cu—27.96NiO—57.04Fe <sub>2</sub> O <sub>3</sub>	0.180	0.1	0.03	0.05
15	1Ag—14Cu—27.96NiO—57.04Fe <sub>2</sub> O <sub>3</sub>	0.175	0.12	0.04	0.06
16	1Ag—14Cu—27.96NiO—57.04Fe <sub>2</sub> O <sub>3</sub>	0.203	0.08	0.02	0.1
17	1Ag—14Cu—27.96NiO—57.04Fe <sub>2</sub> O <sub>3</sub>	0.230	0.12	0.01	0.04
18	1Ag—14Cu—27.96NiO—57.04Fe <sub>2</sub> O <sub>3</sub>	0.184	0.17	0.18	0.47
19	1Ag—14Cu—27.96NiO—57.04Fe <sub>2</sub> O <sub>3</sub>	0.193	0.29	0.044	0.44
20	1Ag—14Cu—5ZnO—28.08NiO—56.92Fe <sub>2</sub> O <sub>3</sub>	0.201	0.16	0.02	0.02
21	1Ag—14Cu—27.96NiO—57.04Fe <sub>2</sub> O <sub>3</sub>	0.144	0.44	0.092	0.15
22	1Ag—14Cu—5ZnO—28.08NiO—56.92Fe <sub>2</sub> O <sub>3</sub>	0.191	0.48	0.046	0.17
23	1Ag—14Cu—5ZnO—28.08NiO—56.92Fe <sub>2</sub> O <sub>3</sub>	0.214	0.185	0.04	0.047
24	1Ag—14Cu—27.96NiO—57.04Fe <sub>2</sub> O <sub>3</sub>	0.201	0.15	0.06	0.123
25	1Ag—14Cu—5ZnO—28.08NiO—56.92Fe <sub>2</sub> O <sub>3</sub>	0.208	0.22	0.05	0.08
26	1Ag—14Cu—27.96NiO—57.04Fe <sub>2</sub> O <sub>3</sub>	0.201	0.18	0.03	0.08
27	1Ag—14Cu—5ZnO—28.08NiO—56.92Fe <sub>2</sub> O <sub>3</sub>	0.252	0.21	0.05	0.08
28	1Ag—14Cu—27.96NiO—57.04Fe <sub>2</sub> O <sub>3</sub>	0.203	0.21	0.057	0.123
29	1Ag—14Cu—27.35NiO—55.95Fe <sub>2</sub> O <sub>3</sub> —1.7ZnO	0.251	0.12	0.03	0.043
30	1Ag—14Cu—27.96NiO—57.04Fe <sub>2</sub> O <sub>3</sub>	0.238	0.12	0.05	0.184
31	1Ag—14Cu—27.96NiO—57.04Fe <sub>2</sub> O <sub>3</sub>	0.221	0.185	0.048	0.157
32	1Ag—14Cu—27.35NiO—55.95Fe <sub>2</sub> O <sub>3</sub> —1.7ZnO	0.256	0.16	0.019	0.028
33	1Pd—15Cu—40.48Fe <sub>2</sub> O <sub>3</sub> —43.32NiO—0.2ZnO	0.149	0.11	0.01	0.024
34	1Ag—14Cu—27.96NiO—57.04Fe <sub>2</sub> O <sub>3</sub>	0.241	0.186	0.05	0.22
35	3Pd—14Cu—42.91NiO—40.09Fe <sub>2</sub> O <sub>3</sub>	0.107	0.2	0.02	0.11
36	1Pt—15Cu—57.12Fe <sub>2</sub> O <sub>3</sub> —26.88NiO	0.105	0.14	0.024	0.041
37	1Pd—15Cu—57Fe <sub>2</sub> O <sub>3</sub> —27.8NiO—0.2ZnO	0.279	0.115	0.014	0.023
38	1Pd—15Cu—40.48Fe <sub>2</sub> O <sub>3</sub> —43.32NiO—0.2ZnO	0.191	0.116	0.031	0.038
39	1Pd—15Cu—40.48Fe <sub>2</sub> O <sub>3</sub> —43.32NiO—0.2ZnO	0.253	0.115	0.07	0.085
40	0.5Pd—16Cu—43.27NiO—40.43Fe <sub>2</sub> O <sub>3</sub> —0.2ZnO	0.129	0.096	0.042	0.06
41	0.5Pd—16Cu—43.27NiO—40.43Fe <sub>2</sub> O <sub>3</sub> —0.2ZnO	0.137	0.113	0.033	0.084
42	0.1Pd—0.9Ag—15Cu—43.32NiO—40.48Fe <sub>2</sub> O <sub>3</sub> —0.2ZnO		0.18	0.04	0.066
43	0.05Pd—0.95Ag—14Cu—27.9NiO—56.9Fe <sub>2</sub> O <sub>3</sub> —0.2ZnO	0.184	0.038	0.013	0.025
44	0.1Pd—0.9Ag—14Cu—27.9NiO—56.9Fe <sub>2</sub> O <sub>3</sub> —0.2ZnO	0.148	0.18	0.025	0.05
45	0.1Pd—0.9Ag—14Cu—27.35NiO—55.95Fe <sub>2</sub> O <sub>3</sub> —1.7ZnO	0.142	0.09	0.02	0.03
46	0.05Pd—0.95Ag—14Cu—27.35NiO—55.95Fe <sub>2</sub> O <sub>3</sub> —1.7ZnO	0.160	0.35	0.052	0.084
47	1Ru—14Cu—27.35NiO—55.95Fe <sub>2</sub> O <sub>3</sub> —1.7ZnO	0.215	0.27	0.047	0.081
48	0.1Pd—0.9Ag—14Cu—55.81Fe <sub>2</sub> O <sub>3</sub> —27.49NiO—1.7ZnO	0.222	0.31	0.096	0.18
49	1.86Ag(as Ag <sub>2</sub> O)—14.02Cu—27.21NiO—55.23Fe <sub>2</sub> O <sub>3</sub> —1.68ZnO	0.147	0.15	0.008	0.027
50	0.1Pd—2.7Ag(as Ag <sub>2</sub> O)—14.02Cu—26.9NiO—54.6Fe <sub>2</sub> O <sub>3</sub> —1.66ZnO	0.180	0.17	0.03	0.049
51	0.1Pd—0.9Ag(as Ag <sub>2</sub> O)—14Cu—25.49NiO—55.81Fe <sub>2</sub> O <sub>3</sub> —1.7ZnO	0.203	0.2	0.05	0.03
52	1.86Ag(as Ag <sub>2</sub> O)—14.02Cu—27.21NiO—55.23Fe <sub>2</sub> O <sub>3</sub> —1.68ZnO	0.279	0.27	0.06	0.36
53	0.1Pd—0.9Ag(as Ag <sub>2</sub> O)—14Cu—25.49NiO—55.81Fe <sub>2</sub> O <sub>3</sub> —1.7ZnO	0.179	0.07	0.023	0.02
54	1.86Ag(as Ag <sub>2</sub> O)—14.02Cu—27.21NiO—55.23Fe <sub>2</sub> O <sub>3</sub> —1.68ZnO	0.321	0.15	0.05	0.028
55	1.86Ag(as Ag <sub>2</sub> O)—14.02Cu—27.21NiO—55.23Fe <sub>2</sub> O <sub>3</sub> —1.68ZnO	0.212	0.19	0.02	0.075
56	1.86Ag(as Ag <sub>2</sub> O)—14.02Cu—27.21NiO—55.23Fe <sub>2</sub> O <sub>3</sub> —1.68ZnO	0.194	0.13	0.01	0.02
57	1.0Ag(as Ag <sub>2</sub> O)—14Cu(as CuO)—27.5NiO—55.8Fe <sub>2</sub> O <sub>3</sub> —1.7ZnO	0.202	0.12	0.023	0.03
58	1.86Ag(as Ag <sub>2</sub> O)—14.02Cu—27.21NiO—55.23Fe <sub>2</sub> O <sub>3</sub> —1.68ZnO	0.241	0.10	0.01	0.02

The results in Table 4 show low levels of contamination in the aluminum produced with the inert anodes, particularly for anodes comprising iron, nickel and zinc oxides. In accordance with the present invention, the presence of a controlled amount of ZnO is believed to reduce the solubility of NiO in the electrolyte bath, thereby reducing the amount of Ni contamination in the aluminum produced in the bath. In addition, the inert anode wear rate was extremely low in each sample tested. Optimization of processing parameters and cell operation may further improve the purity of aluminum produced in accordance with the invention.

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The present inert anode compositions are particularly useful in electrolytic cells for aluminum production operated at temperatures in the range of about 800–1,000° C. A particularly preferred cell operates at a temperature of about 900–980° C., preferably about 930–970° C. An electric current is passed between the inert anode and a cathode through a molten salt bath comprising an electrolyte and an oxide of the metal to be collected. In a preferred cell for aluminum production, the electrolyte comprises aluminum fluoride and sodium fluoride and the metal oxide is alumina. The weight ratio of sodium fluoride to aluminum fluoride is about 0.7 to 1.25, preferably about 1.0 to 1.20. The electrolyte may also contain calcium

While the invention has been described in terms of preferred embodiments, various changes, additions and modifications may be made without departing from the scope of the invention as set forth in the following claims.

What is claimed is:

1. An inert anode composition for use in a molten salt bath, the composition comprising nickel, iron and zinc oxide, wherein the amounts of nickel, iron and zinc in the composition correspond to the following mole fractions of NiO, Fe<sub>2</sub>O<sub>3</sub> and ZnO: 0.2 to 0.99 NiO; 0.0001 to 0.8 Fe<sub>2</sub>O<sub>3</sub>; and 0.0001 to 0.3 ZnO.
2. The inert anode composition of claim 1, wherein the mole fraction of NiO is from 0.45 to 0.8, the mole fraction of Fe<sub>2</sub>O<sub>3</sub> is from 0.05 to 0.499, and the mole fraction of ZnO is from 0.001 to 0.26.
3. The inert anode composition of claim 1, wherein the mole fraction of NiO is from 0.45 to 0.65, the mole fraction of Fe<sub>2</sub>O<sub>3</sub> is from 0.2 to 0.49, and the mole fraction of ZnO is from 0.001 to 0.22.
4. The inert anode composition of claim 1, wherein the mole fraction of ZnO is from 0.05 to 0.30.
5. The inert anode composition of claim 1, wherein the composition comprises the nominal formula Ni<sub>1.17</sub>Zn<sub>0.08</sub>Fe<sub>1.5</sub>O<sub>4</sub>.
6. The inert anode composition of claim 1, wherein the composition comprises the nominal formula Ni<sub>1.1</sub>Zn<sub>0.17</sub>Fe<sub>1.5</sub>O<sub>4</sub>.
7. The inert anode composition of claim 1, wherein the composition comprises the nominal formula Ni<sub>1.5</sub>Zn<sub>0.5</sub>FeO<sub>4</sub>.
8. The inert anode composition of claim 1, wherein the composition comprises the nominal formula Ni<sub>1.1</sub>Zn<sub>0.1</sub>Fe<sub>1.8</sub>O<sub>4</sub>.
9. The inert anode composition of claim 1, wherein the composition comprises the nominal formula Ni<sub>0.95</sub>Zn<sub>0.12</sub>Fe<sub>1.9</sub>O<sub>4</sub>.
10. The inert anode composition of claim 1, wherein the composition is made from NiO, Fe<sub>2</sub>O<sub>3</sub> and ZnO, or precursors thereof.
11. The inert anode composition of claim 1, wherein the composition further comprises at least one metal selected from Cu, Ag, Pd, Pt, Au, Rh, Ru, Ir and Os.
12. The inert anode composition of claim 11, wherein the at least one metal is selected from Cu, Ag, Pd, Pt and combinations thereof.
13. The inert anode composition of claim 1, wherein the composition has a Hall cell bath solubility of less than 0.1 weight percent total dissolved oxides.
14. The inert anode composition of claim 1, wherein the composition has a Hall cell bath solubility of less than 0.08 weight percent total dissolved oxides.
15. The inert anode composition of claim 1, wherein the composition has a Hall cell bath solubility of less than 0.075 weight percent total dissolved oxides.
16. The inert anode composition of claim 1, wherein the composition has a Hall cell bath solubility of less than 0.03 weight percent NiO.
17. The inert anode composition of claim 1, wherein the composition has a Hall cell bath solubility of less than 0.025 weight percent NiO.
18. The inert anode composition of claim 1, wherein the composition has a Hall cell bath solubility of less than 0.075 weight percent total dissolved oxides, and a Hall cell bath solubility of less than 0.03 weight percent NiO.
19. The inert anode composition of claim 1, wherein the composition has a Hall cell bath solubility of less than 0.075 weight percent total dissolved oxides, and a Hall cell bath solubility of less than 0.025 weight percent NiO.

20. A method of making an inert anode composition, the method comprising:

mixing nickel oxide, iron oxide and zinc oxide or precursors thereof; and

calcining the mixture to form a ceramic material comprising nickel, iron and zinc oxide, wherein the amounts of nickel, iron and zinc in the composition correspond to the following mole fractions of NiO, Fe<sub>2</sub>O<sub>3</sub> and ZnO: 0.2 to 0.99 NiO; 0.0001 to 0.8 Fe<sub>2</sub>O<sub>3</sub>; and 0.0001 to 0.3 ZnO.

21. The method of claim 20, wherein the mole fraction of NiO is from 0.45 to 0.8, the mole fraction of Fe<sub>2</sub>O<sub>3</sub> is from 0.05 to 0.499, and the mole fraction of ZnO is from 0.001 to 0.26.

22. The method of claim 20, wherein the mole fraction of NiO is from 0.45 to 0.65, the mole fraction of Fe<sub>2</sub>O<sub>3</sub> is from 0.2 to 0.49, and the mole fraction of ZnO is from 0.001 to 0.22.

23. The method of claim 20, wherein the mole fraction of ZnO is from 0.05 to 0.30.

24. The method of claim 20, wherein the ceramic material comprises the nominal formula Ni<sub>1.17</sub>Zn<sub>0.08</sub>Fe<sub>1.5</sub>O<sub>4</sub>.

25. The method of claim 20, wherein the ceramic material comprises the nominal formula Ni<sub>1.1</sub>Zn<sub>0.17</sub>Fe<sub>1.5</sub>O<sub>4</sub>.

26. The method of claim 20, wherein the ceramic material comprises the nominal formula Ni<sub>1.5</sub>Zn<sub>0.5</sub>FeO<sub>4</sub>.

27. The method of claim 20, wherein the ceramic material comprises the nominal formula Ni<sub>1.1</sub>Zn<sub>0.1</sub>Fe<sub>1.8</sub>O<sub>4</sub>.

28. The method of claim 20, wherein the ceramic material comprises the nominal formula Ni<sub>0.95</sub>Zn<sub>0.12</sub>Fe<sub>1.9</sub>O<sub>4</sub>.

29. The method of claim 20, wherein the nickel oxide, iron oxide and zinc oxide are provided from NiO, Fe<sub>2</sub>O<sub>3</sub> and ZnO.

30. The method of claim 20, wherein at least one of the nickel oxide, iron oxide and zinc oxide are provided from at least one compound selected from the group comprising chlorides, acetates, nitrates, tartarates, citrates and sulfates of Ni, Fe and Zn salts.

31. An electrolytic cell for producing metal comprising: a molten salt bath comprising an electrolyte and an oxide of a metal to be collected;

a cathode; and

an inert anode comprising nickel, iron and zinc oxide, wherein the amounts of nickel, iron and zinc in the composition correspond to the following mole fractions of NiO, Fe<sub>2</sub>O<sub>3</sub> and ZnO: 0.2 to 0.99 NiO; 0.0001 to 0.8 Fe<sub>2</sub>O<sub>3</sub>; and 0.0001 to 0.3 ZnO.

32. The electrolytic cell of claim 31, wherein the mole fraction of NiO is from 0.45 to 0.8, the mole fraction of Fe<sub>2</sub>O<sub>3</sub> is from 0.05 to 0.499, and the mole fraction of ZnO is from 0.001 to 0.26.

33. The electrolytic cell of claim 31, wherein the mole fraction of NiO is from 0.45 to 0.65, the mole fraction of Fe<sub>2</sub>O<sub>3</sub> is from 0.2 to 0.49, and the mole fraction of ZnO is from 0.001 to 0.22.

34. The electrolytic cell of claim 31, wherein the mole fraction of ZnO is from 0.05 to 0.30.

35. A method of producing commercial purity aluminum comprising:

passing current between an inert anode and a cathode through a bath comprising an electrolyte and aluminum oxide, wherein the inert anode comprises nickel, iron and zinc oxide, wherein the amounts of nickel, iron and zinc in the composition correspond to the following mole fractions of NiO, Fe<sub>2</sub>O<sub>3</sub> and ZnO: 0.2 to 0.99 NiO; 0.0001 to 0.8 Fe<sub>2</sub>O<sub>3</sub>; and 0.0001 to 0.3 ZnO; and



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recovering aluminum comprising a maximum of 0.20 weight percent Fe, 0.1 weight percent Cu, and 0.034 weight percent Ni.

36. The method of claim 35, wherein the mole fraction of NiO is from 0.45 to 0.8, the mole fraction of  $\text{Fe}_2\text{O}_3$  is from 0.05 to 0.499, and the mole fraction of ZnO is from 0.001 to 0.26.

37. The method of claim 35, wherein the mole fraction of NiO is from 0.45 to 0.65, the mole fraction of  $\text{Fe}_2\text{O}_3$  is from 0.2 to 0.49, and the mole fraction of ZnO is from 0.001 to 0.22.

38. The method of claim 35, wherein the mole fraction of ZnO is from 0.05 to 0.30.

39. The method of claim 35, wherein the inert anode comprises the nominal formula  $\text{Ni}_{1.17}\text{Zn}_{0.08}\text{Fe}_{1.5}\text{O}_4$ .

40. The method of claim 35, wherein the inert anode comprises the nominal formula  $\text{Ni}_{1.1}\text{Zn}_{0.17}\text{Fe}_{1.5}\text{O}_4$ .

41. The method of claim 35, wherein the inert anode comprises the nominal formula  $\text{Ni}_{1.5}\text{Zn}_{0.5}\text{FeO}_4$ .

42. The method of claim 35, wherein the inert anode comprises the nominal formula  $\text{Ni}_{1.1}\text{Zn}_{0.1}\text{Fe}_{1.8}\text{O}_4$ .

43. The method of claim 35, wherein the inert anode comprises the nominal formula  $\text{Ni}_{0.95}\text{Zn}_{0.12}\text{Fe}_{1.9}\text{O}_4$ .

44. The method of claim 35, wherein the recovered aluminum comprises a maximum of 0.15 weight percent Fe, 0.034 weight percent Cu, and 0.03 weight percent Ni.

45. The method of claim 35, wherein the recovered aluminum comprises a maximum of 0.13 weight percent Fe, 0.03 weight percent Cu, and 0.03 weight percent Ni.

46. The method of claim 35, wherein the recovered aluminum further comprises a maximum of 0.2 weight percent Si, 0.03 weight percent Zn, and 0.03 weight percent Co.

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47. The method of claim 35, wherein the recovered aluminum comprises a maximum of 0.10 weight percent of the total of the Cu, Ni and Co.

48. The method of claim 35, wherein the nickel, iron and zinc oxide has a Hall cell bath solubility of less than 0.1 weight percent total dissolved oxides.

49. The method of claim 35, wherein the nickel, iron and zinc oxide has a Hall cell bath solubility of less than 0.08 weight percent total dissolved oxides.

50. The method of claim 35, wherein the nickel, iron and zinc oxide has a Hall cell bath solubility of less than 0.075 weight percent total dissolved oxides.

51. The method of claim 35, wherein the nickel, iron and zinc oxide has a Hall cell bath solubility of less than 0.03 weight percent NiO.

52. The method of claim 35, wherein the nickel, iron and zinc oxide has a Hall cell bath solubility of less than 0.025 weight percent NiO.

53. The method of claim 35, wherein the nickel, iron and zinc oxide has a Hall cell bath solubility of less than 0.075 weight percent total dissolved oxides, and a Hall cell bath solubility of less than 0.03 weight percent NiO.

54. The method of claim 35, wherein the nickel, iron and zinc oxide has a Hall cell bath solubility of less than 0.075 weight percent total dissolved oxides, and a Hall cell bath solubility of less than 0.025 weight percent NiO.

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